COMBUSTION CHEMISTRY OF PROPANE: A CASE STUDY OF DETAILED REACTION MECHANISM OPTIMIZATION

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Detailed chemical reaction mechanisms describing hydrocarbon combustion chemistry are conceptually structured in a hierarchical manner with H_2 and CO chemistry at the base, supplemented as needed by elementary reactions of larger chemical species. While this structure gives a logical organization to combustion chemistry, the degree to which this organization reflects actual reactive fluxes in flames is not known. Moreover, it has not been tested whether sets of rate parameters derived by optimizing fits to small-hydrocarbon combustion data are secure foundations upon which to optimize the rate parameters needed for modeling the combustion of larger hydrocarbons. In this work, a computer modeling study was undertaken to discover whether optimizing the rate parameters of a 258-reaction C_3 combustion chemistry mechanism that was added to a previously optimized 205-reaction $C_{<3}$ mechanism would provide satisfactory accounting for C_3 flame speed and ignition data. The optimization was done with 21 optimization targets, 9 of which were ignition delays and 12 of which were atmospheric pressure laminar flame speeds; 2 of the ignition delays and 2 of the flame speeds, all for methane fuel, had served as optimization targets for the $C_{<3}$ rate parameters. It was found in sensitivity studies that the coupling between the C_3 and the $C_{<3}$ chemistry was much stronger than anticipated. No set of C_3 rate parameters could account for the C_3 combustion data as long as the previously optimized (against $C_{<3}$ optimization targets only) $C_{<3}$ rate parameters remained fixed. A reasonable match to the C_3 targets could be obtained, without degrading the match between experiment and calculation for the $C_{<3}$ optimization targets, by reoptimizing six of the previously optimized and three additional $C_{<3}$ rate parameters.

Introduction

Computer models for combustion processes may include a detailed chemical reaction model. Because the rate constants of elementary gas-phase reactions are restricted to ranges governed by a well-understood theory of elementary gas reaction rates [1], more confidence can be placed in simulations based on well-parameterized detailed combustion chemistry models than in simulations done using summary combustion chemistry models with parameters derived by fitting data for conditions that are often quite different from those of interest for the simulation. However, most elementary reaction rate parameters are not known with sufficient accuracy for this purpose, so detailed models still have to be calibrated one way or another against combustion data.

Detailed reaction mechanisms describing hydrocarbon combustion chemistry have hierarchical structures with H_2 and CO chemistry at the base, supplemented as needed by reaction channels of larger chemical species. While such structures provide rational organization of elementary reactions, it is unknown whether they may in some way reflect actual reactive fluxes. Moreover, it has not been tested whether parameter sets derived by optimizing smaller-hydrocarbon mechanisms are secure foundations for optimizing the rate parameters needed for modeling the combustion of larger fuel molecules. We studied these questions with a model comprising a 258-reaction C_3 mechanism, described below, and a thoroughly validated $C_{<3}$ model taken from the literature [2]. While our focus was on propane combustion, the parameter optimization targets included experiments with additional fuels. Model predictions were eventually tested against CH_4, C_2H_4, C_2H_6, C_3H_4, C_3H_6, and C_3H_8 laminar flame speed and shock tube ignition delay data.

The optimized parameter sets and implications for small-hydrocarbon combustion modeling are discussed.

TABLE 1
Target set and results of optimizations

No.	%	Target	T/K	ϕ	P/atm	Value Exp	Base	Final	Optimization Results[a] A	B	C	D	E	Ref.
Ignition delays (μs) in shock-heated fuel/oxygen/argon mixtures														
1	33	CH_4	1600	5	3.80	335	315	328	−6	−5	−6	−3	−4	[8]
2	9.1	CH_4	1700	1	2.04	105	111	116	6	8	6	9	9	[8]
3	1	a-C_3H_4	1325	0.5	3.44	503	850	567	2	0	2	2	1	[9]
4	1	a-C_3H_4	1590	2	3.52	281	225	240	−3	−3	−3	−3	−3	[9]
5	1	p-C_3H_4	1360	0.5	3.51	394	385	410	2	−1	2	−1	2	[9]
6	1	p-C_3H_4	1470	1	3.42	348	320	335	−3	0	1	−3	1	[9]
7	0.15	C_3H_8	1460	0.75	3.95	375	295	370	−3	−2	−3	−3	−3	[11]
8	0.20	C_3H_8	1460	1	4.09	475	384	480	2	1	2	2	3	[11]
9	0.15	C_3H_8	1600	0.75	3.88	77	72	80	2	10	4	5	5	[11]
Laminar flame speeds (cm/s) in fuel/air mixtures at P = 1 atm														
10		CH_4		0.98		35.5	37.8	35.4	6	−6	6	2	−3	[12]
11		CH_4		1.43		12.4	12.7	11.9	1	5	1	−2	1	[12]
12		C_2H_4		0.8		47.8	64.1	49.2	35	−2	29	5	2	[13]
13		C_2H_4		1.2		71.9	91.3	73.8	27	−1	19	5	−1	[13]
14		C_2H_6		.75		23.0	28.0	24.1	21	9	21	11	11	[12]
15		C_2H_6		1.25		40.0	37.8	35.2	−7	−5	−9	−9	−7	[12]
16		p-C_3H_4		0.8		31.1	38.9	35.5	24	7	24	17	12	[6][b]
17		p-C_3H_4		1.2		44.7	48.7	47.2	9	1	9	8	3	[6][b]
18		C_3H_6		0.8		32.1	34.4	30.8	−4	1	−1	−1	1	[5]
19		C_3H_6		1.2		45.8	44.3	42.7	−8	−4	−8	−5	−4	[5]
20		C_3H_8		0.8		29.9	35.2	29.7	4	0	6	3	2	[12]
21		C_3H_8		1.2		40.0	44.7	40.1	2	5	1	4	4	[12]
		Squared fractional residual sum ×1000							335	47	264	82	53	[c]
		Optimized objective function ×1000							322	18	250	65	36	

[a]As percent differences from the experimental values. The optimization keys are: A, All Ref. [2] parameters frozen; B, all optimization parameters free; C, all Ref. [2] parameters frozen except A-factors free for C_2H_4 + O → CH_3 + HCO, C_2H_3 + H → H_2 + C_2H_2, and C_2H_4 + O → H + CH_2CHO; D, as optimization C, plus six of the Ref. [2] parameters free (see text and Fig. 1); E, as optimization D, with three additional Ref. [2] parameters free (see text and Fig. 1).

[b]Measured in N_2-diluted air with 18% N_2 and 21% O_2.

[c]Defined as $\Sigma[1 - T_i(\text{calc})/T_i(\text{expt})]^2$, where the sum is over the 21 target values T_i.

Method

The C_3 component of the mechanism used for this work included reactions of all relevant isomeric forms of C_3H_n with $2 \leq n \leq 8$. For reasons discussed below, chemistry suited to describe reactions of species with up to six C atoms was also included. The total number of additional species was 34; the total number of reactions in the mechanism was 463. (There is a measure of arbitrariness in counting the number of elementary reactions; the count given is that reported by the CHEMKIN programs [3,4].)

Reactions 1–240, 265, 267–278, and 283–285 in Ref. [5] and their rate parameters, distilled from earlier reviews and mechanism proposals as described before [5–7], were used for the C_3 component of the base mechanism. The $C_{<3}$ component of the mechanism was created by removing the nitrogen and propane chemistry parts of the mechanism reported by Smith et al. [2]. The mechanism resulting from one of the optimizations (D), discussed in the following sections, together with the corresponding CHEMKIN-formatted [3,4] thermochemistry and transport property files, can be found at http://ignis.me.udel.edu/propane and http://www.phys.cm.utexas.edu/propane.

The target sources initially considered included all of the ignition and flame-speed data known to us. For the optimization process, this was narrowed, with the help of preliminary sensitivity scans, to the set given in Table 1 [5–6,8–13]. In selecting the laminar flame speed target values for CH_3CCH and C_3H_6, a choice had to be made between the alternative extrapolation methods used to find stretch-free flame-speed values. We adopted the values given by the linear extrapolation method, about 2

Reaction	Ignition CH4		aC3H4	pC3H4		C3H6	C3H8			Flame speed C3H6		CH4			C2H4	C2H6		C3H4	C3H6	C3H8		Optimized X_i values A	B	C	D	E	Span (f_i)
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	A	B	C	D	E	(f_i)
$C_3H_8 + H \rightarrow H_2 + iC_3H_7$																						100	−36	100	100	68	2
$C_3H_6 + OH \rightarrow aC_3H_5 + H_2O$																						86	−83	74	36	−97	2
$C_3H_6 + H \rightarrow aC_3H_5 + H_2$																						−100	−87	−100	−100	−85	2
$C_3H_6 + H \rightarrow C_2H_4 + CH_3$																						−69	−23	−24	52	53	2.5
$aC_3H_5 + H(+M) \rightarrow C_3H_6(+M)$																						39	−80	52	56	82	3
$pC_3H_4 + O \rightarrow C_2H_4 + CO$																						−100	−71	−100	−80	−99	2
$pC_3H_4 + O \rightarrow HCCO + CH_3$																						100	8	100	93	−70	3
$pC_3H_4 \rightarrow aC_3H_4$																						98	8	100	100	100	2
$C_3H_3 + C_3H_3 \rightarrow C_6H_6$																						−34	−94	97	96	−15	3
$C_3H_3 + C_3H_3 \rightarrow C_6H_5 + H$																						−71	78	51	65	98	3
$C_3H_3 + HO_2 \rightarrow pC_3H_4 + O_2$																						−99	−92	−100	−76	−86	3
$C_3H_3 + HO_2 \rightarrow aC_3H_4 + O_2$																						100	100	100	100	99	3
$C_3H_3 + O_2 \rightarrow CH_2CO + HCO$																						59	−2	41	47	39	2
$C_3H_3 + OH \rightarrow C_3H_2 + H_2O$																						96	−63	−100	−49	18	2
$C_3H_3 + H \rightarrow aC_3H_4$																						−100	−96	−100	−100	−98	3
$C_3H_3 + H \rightarrow pC_3H_4$																						−42	−100	−38	−51	−100	3
$C_2H_5 + O_2 \rightarrow HO_2 + C_2H_4$																						−2					5
$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$																							−84		−100	−99	2
$C_2H_4 + O \rightarrow H + CH_2CHO$																							−67	−100	−100	−99	2
$C_2H_4 + O \rightarrow CH_3 + HCO$																							−30	100	100	65	2
$C_2H_4 + H(+M) \rightarrow C_2H_5(+M)$																						97			34	66	3
$C_2H_3 + O_2 \rightarrow O + CH_2CHO$																							−92		−100	−97	2.5
$C_2H_3 + H \rightarrow H_2 + C_2H_2$																							21	100	1	22	2
$C_2H_5 + CH_3(+M) \rightarrow C_3H_8(+M)$																						59	−94	67	97	−4	2
$C_2H_2 + CH_3 \rightarrow pC_3H_4 + H$																						−100	−87	−100	−100	−99	2
$CH_3 + CH_3(+M) \rightarrow C_2H_6(+M)$																						−57					2
$CH_3 + O_2 \rightarrow OH + CH_2O$																						−52					3
$CH_3 + O_2 \rightarrow O + CH_3O$																						34					2
$CH_3 + HO_2 \rightarrow OH + CH_3O$																						−49			−25	−25	3
$CH_3 + HO_2 \rightarrow O_2 + CH_4$																						−33					3
$CH_3 + OH \rightarrow {}^1CH_2 + H_2O$																						−65					3
$CH_3 + H(+M) \rightarrow CH_4(+M)$																						−25					2
$CH_2 + O_2 \rightarrow CO_2 + H + H$																						−72					2
$HCO + M \rightarrow H + CO + M$																						−63			−100		2
$HCO + H_2O \rightarrow H + CO + H_2O$																						−32				−99	1.7
$HCO + H \rightarrow H_2 + CO$																						−7				−53	2.5
$HO_2 + H \rightarrow OH + OH$																						−95		−100	−100		2
$HO_2 + H \rightarrow O_2 + H_2$																						98		100	100		3*

Slower combustion   Faster combustion

Response sensitivity, ×10 for ignition and ×100 for flame speed.   ≤ −5   0   ≥ 5
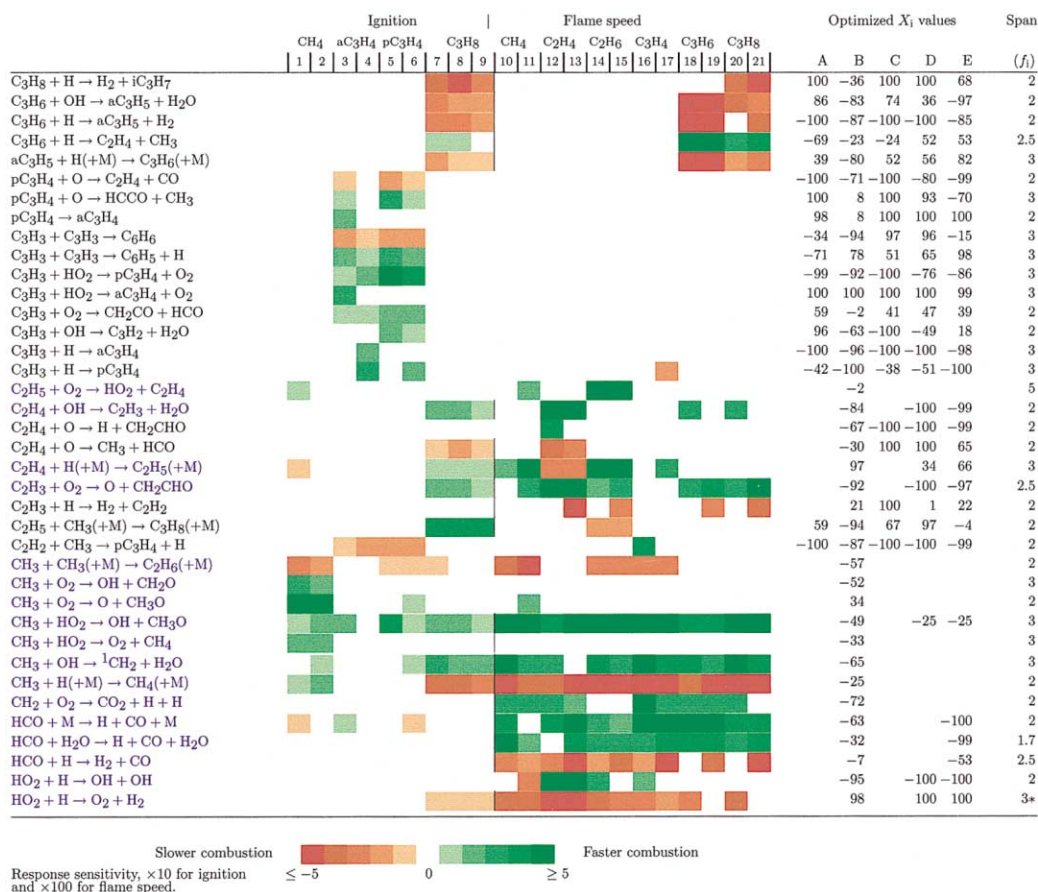
FIG. 1. Sensitivity spectrum and parameter sets derived from the illustrative optimizations (A–E) described in the text and in the footnote to Table 1. Reactions that provided optimization parameters for the $C_{<3}$ component of the model are shown in blue. The sensitivities shown are the normalized or logarithmic response sensitivities [1] of observable quantity i to the rate of reaction j. They were defined for this investigation by $S_{ij} = \partial \ln(s_{u,i})/\partial \ln(A_j)$, where the $s_{u,i}$ were stretch-free atmospheric pressure flame speeds, and by $S_{ij} = \ln(\tau_i(A_j \times 2)/\tau_i(A_j/2))/\ln(4)$, where the τ_i were shock tube ignition delays, and the rate parameters A_j, which were varied by factors of 2 and 1/2 for the ignition sensitivity survey and later optimized, were the Arrhenius A-factors of the elementary reactions listed. All sensitivities greater than 0.05 for ignition and 0.01 for flame speed are shown here and were included in the optimization except for the very sensitive reactions $H + O_2 \rightarrow OH + O$ and $OH + CO \rightarrow CO_2 + H$, the rate constants for which are felt to be well known [15,16] and were taken as fixed for the purpose of this investigation. The optimized X_i values are given as signed percentages of the spans listed in the final column; thus the optimized A-factor for reaction i is given by $A_{i,\mathrm{opt}} = f_i^{X_i/100} A_{i,\mathrm{base}}$. Blank entries in the X_i columns correspond to fixed parameters. The left-to-right order of targets here corresponds to the top-to-bottom order of Table 1.* The span for $HO_2 + H \rightarrow O_2 + H_2$ was 3 for optimization B and 1.73 for optimizations D and E.

cm/s greater than values given by the nonlinear extrapolation method, at the limit of the uncertainty range of the laser Doppler velocimetry (LDV) measurement in the experiments. Because the base mechanism studied in this work generally overpredicts laminar flame speeds, this choice has the effect of narrowing the difference between experiment and prediction that is to be removed by the optimization process.

Ignition calculations were done using the CHEM-KIN programs [3] and locally written programs for integrating the initial-value problem corresponding to adiabatic reaction at constant density starting at the full thermal relaxation, with no chemical reaction conditions computed from incident shock speed and the conservation equations appropriate to ideal shock-wave reflection [14]. Ignition was defined as the time between reflected shock heating and

maximum rate of pressure rise. Flame modeling was done using the PREMIX program [4].

Sensitivity scanning for ignition delay was done using the brute force method and factors of 2 A-factor changes for the entire base mechanism and all targets initially considered. For flame speeds, local sensitivity calculations were used for extensive exploration of the chemistry involved. Finally, critical analysis of matches between computation and experiment provided the overview of the experimental data base needed to choose targets for systematic parameter optimization. A thermochemical sensitivity investigation was not carried out. The sensitivity spectrum is shown in Fig. 1 [15,16].

The optimization approach and protocol were essentially identical to the one used by Smith et al. [2]. Briefly, the 21 target values η_i, either flame speeds or ignition delays, were expressed as second-order polynomials $\ln \eta_i = a_i + \Sigma b_{ij} X_{ij} + \Sigma c_{ijk} X_{ij} X_{ik}$, where the second sum is taken for $j \leq k$ and the coefficients a, b, and c were evaluated by regression of a factorial design test extended over all sensitive combinations of target and reaction for the "uncertainty spans" f (Fig. 1) assigned to the base-mechanism A-factors based upon critical review of the elementary reaction literature. The 38 optimization variables were scaled by the transformation $X = \ln(A/A_{\text{base}})/\ln(f)$; optimal $\{X_i\}$ sets were located as best local minima of the objective function $\Sigma[1 - \eta_i(\text{calc})/\eta_i(\text{expt})]^2$ subject to the constraint $-1 < X_i < +1$. In final optimization rounds, a modification was made to the objective function by removing contributions to the sum from targets that were matched to within error bounds of 10 μs (ignition delays), ± 1 cm/s for unstretched flame speeds [12], and $+0/-2$ cm/s for flame speeds measured by linear extrapolation to zero stretch [5,6,13]. In order to preserve the smoothness of the response function, these error bounds were expressed by reducing the contributions from terms within but still near the error limits by appropriately scaled $\exp(-(x/\alpha)^2)$ functions, with $\alpha = 0.1$ for both ignition data and flame speeds in the optimizations shown in Table 1 and Fig 1.

Results

An overview of optimization results found in five illustrative optimizations, discussed below, is given in Table 1 and Fig. 1.

In initial, unsystematic, searches for improvements in the base mechanism that could improve the matches to C_3 data, two basic facts became clear. The first was that it would not be possible to get model predictions within the scatter of the C_3 data without reconsidering the $C_{<3}$ rate constants that had been optimized against $C_{<3}$ data by Smith et al. [2]. (The sensitive reactions in the $C_{<3}$ component of the model are included in Fig. 1.) In other words,

experience with informal rate constant adjustments of the C_3 chemistry rate parameters, including unreasonably large adjustments, consistently led to the conclusion that C_3 rate-constant optimization alone would be ineffective.

The second was that informal or limited-scope adjustments of the $C_{<3}$ rate constants would not achieve the corrections needed either.

To illustrate these conclusions, the results of five systematic optimizations are shown in Table 1 and Fig. 1. In optimization A, all of the $C_{<3}$ rate constants were frozen; this gave the poor matches to the C_3 data shown in the first results column of Table 1, with a squared residual sum of 34%. For comparison, freeing all of the optimization parameters, in optimization B, leads to a fit within the data scatter for all of the targets and a squared residual sum of 5%. In optimization C, the rate constants that had been optimized for $C_{<3}$ targets were again frozen, while three $C_{<3}$ rate constants that had not been optimized by Smith et al. [2] were free (see caption to Table 1); there was some improvement over optimization A, but again the C_3 data is not matched, and the squared residual sum is an unacceptable 26%.

We then explored how extensively the $C_{<3}$ parameter set would have to be freed in order to approach an acceptable match to the C_3 data. Elementary reactions that promised to provide the most improvement were tested serially until optimizations D and E (Table 1 and Fig. 1) were found to be the best we could obtain with this approach, with 8% and 5% squared residual sums, respectively.

Comparisons with experimental data for flame speeds and ignition delays computed with the rate parameters found in optimization D are shown in Figs. 2 and 3; computed matches to the optimization targets are listed in Table 1.

Discussion

The focus of this study was to discover whether a chemical model rigorously optimized to match $C_{<3}$ combustion data can serve, with the same values for its rate and other parameters, as a base for an expanded reaction mechanism incorporating reactions of larger hydrocarbon species. In an idealized sense, this should be possible. It requires two things: that the $C_{<3}$ chemistry mimic nature faithfully and that its parameters can be optimized against a data array of sufficient size, variety, and sensitivity to determine them all accurately.

$C_{<3}$ chemistry is generally felt to have been explored in sufficient breadth and depth over the past decades to assure that important qualitative additions to it would be quite surprising. Thus, the completeness of current $C_{<3}$ chemistry models is accepted. The sufficiency of the available data for parameter optimization, however, is another matter.
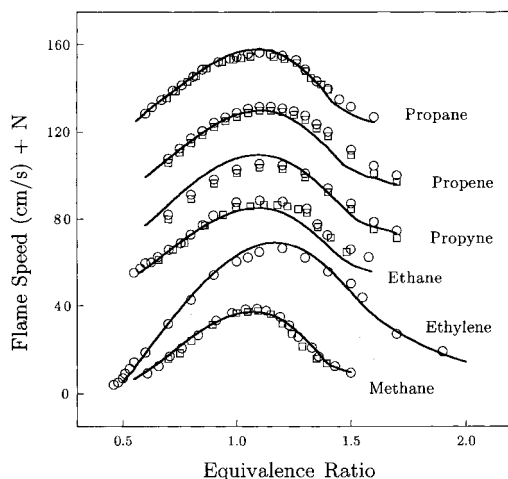
FIG. 2. Atmospheric pressure laminar flame speeds in air calculated with the parameter set resulting from optimization D, offset by N cm/sec, compared to literature data. Methane, $N = 0$, circles [17], squares [12]; ethylene, $N = -5$: [13]; ethane, $N = 45$, circles [17], squares [12]; propyne, $N = 60$, linear (circles) and nonlinear (squares) extrapol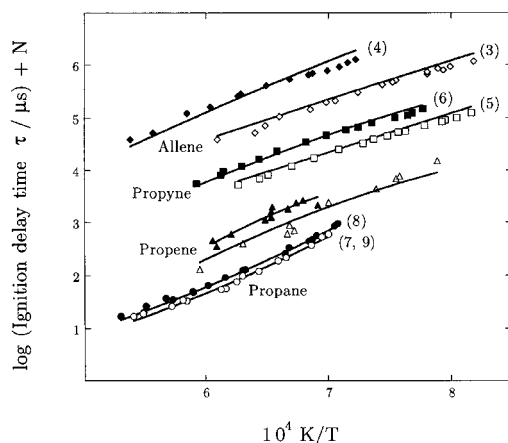ations to zero stretch from [5]; propene, $N = 85$, linear (circles) and nonlinear (squares) extrapolations to zero stretch from [5]; propane, $N = 115$, circles [17], squares [12].

FIG. 3. Calculated ignition delays, offset by N log units, compared to experimental data. The numbers denote the mixture compositions and pressures listed in Table 1; the propene data are for $\phi = 0.5$ and $\phi = 1.0$ experiments by Qin et al. [10] at $P_5 = 4$ atm. Allene, $N = 3$ [9]; propyne, $N = 2$ [9]; propene, $N = 1$ [10]; propane, $N = 0$ [11].

We chose the Smith et al. [2] $C_{<3}$ model for our test specifically because of its rigorous derivation, its thorough theoretical examination of the rate coefficient expressions for all elementary reactions, and its exhaustive validation against data representative of essentially the entire extant literature of high-temperature small-molecule combustion. Our finding that adding C_3 chemistry to it did not lead to acceptable matches to the C_3 data as long as only the C_3 rate parameters were allowed to vary in the optimization does not lead us to doubt the qualitative correctness of their model, nor of the C_3 chemistry we added to it, nor does it cast doubt upon the method used by them or by us for parameter optimization. Instead, it underscores the limited variety, sensitivity, and accuracy of the data that has been collected in combustion and related experiments. There is no reason to believe that any other result would emerge from taking a different currently available $C_{<3}$ model as the base mechanism.

The close matches initially found for methane ignition delays and laminar flame speeds were not unexpected, because these experiments had been used by Smith et al. as optimization targets. With few exceptions, the rest of the comparisons to the target values (in the "Exp" and "Base" columns of Table 1) show that the base model predicts significantly faster combustion, both for flame and for ignition conditions, than found experimentally. The same behavior was also noted for the full range of C_3 combustion data surveyed.

In particular, the unacceptably large flame speeds computed by the base model for ethylene and propyne, which are not sensitive to C_3 chemistry and have similar sensitivities to $C_{<3}$ chemistry, confirm that too-fast $C_{<3}$ chemistry is responsible for the too-fast flame speeds. This conclusion is supported by the results of optimizations B, D, and E, where the $C_{<3}$ rate constants are nearly all consistently forced in the direction of slower combustion (Fig. 1).

The sensitivity tableau of Fig. 1 suggests at first inspection that adjustments to rate constants for reactions of the larger species alone should lead to much closer matches between model predictions and experiment. Table 1 shows, however, that this pertains only to the C_3 ignition delays, and that parameter optimization including only the C_3 reactions (optimization A) fails to find a set of C_3 rate parameters that can account for the laminar flame-speed data.

In other words, the significant sensitivities found for the larger-fuel flame-speed targets are predominantly so tightly coupled to the sensitivities for smaller-fuel targets that a satisfactory simultaneous match is not possible under the constraint of leaving the small-molecule parameters fixed. Freeing the three small-molecule parameters not optimized by Smith et al. (optimization C) did lead to a smaller optimized objective function, but inspection of the

target matches shows that this optimization really did not succeed either.

The question of how many, or which set, of $C_{<3}$ rate parameters should be considered for reoptimization was addressed in this study only to a very limited extent. The limited goal of deriving a combustion model able to reproduce with reasonable accuracy the principal combustion characteristics of the fuels considered here is readily reached by the method we used. Indeed, allowing the parameter sets free in optimizations D and E to vary already gives results that are more than acceptable by current standards, as illustrated in Figs. 2 and 3 for the model from optimization D.

A parameter optimization project can only be deemed fully satisfactory, however, if the optimized parameters behave in a stable and, in the case of a physical model, theoretically reasonable manner. In underdetermined and ill-conditioned parameter optimizations, which rate-constant optimizations for combustion models will be for a long time to come, this goal is extremely difficult to approach. Inspection of the behavior of the $\{X_i\}$ sets in Fig. 1 shows that several of the parameters were consistently driven by the optimization to their allowed limits, a behavior also found by Smith et al. [2]. The reasons for this require further study. Increasing the number of optimization targets would be helpful, but with the rigorous methods used in this investigation, significant expansion of the target set would demand computer resources beyond normal means.

For these reasons, we emphasize that the parameters derived in this study should be understood for what they reveal about parameter optimization in combustion chemistry, not to provide a rigorously optimized and validated model for C_3 and $C_{<3}$ combustion chemistry comparable to the Smith et al. model for $C_{<3}$ combustion chemistry. To achieve the latter would require reoptimization against all of the data used by Smith et al. and against the data used here. Whether such an undertaking would merit the effort is an open question.

Among the important additional issues that have to be addressed in developing a higher-level propane combustion model is the kinetics of the propargyl radical (C_3H_3) self-reactions. In the present model, the product channels forming benzene and phenyl radical were assumed to be normal and reversible elementary reactions [5,7]. This assumption is a reasonable one at our current level of understanding this important reaction, but there are grounds to believe that it may be unsatisfactory because these may not be elementary reactions [18].

While we did not undertake optimizations starting with any other of the detailed reaction mechanisms that have been proposed for small-molecule combustion chemistry [1], it should be evident from the results reported here that similar conclusions are to be expected from any starting point that is based upon current knowledge of the elementary reactions of small-molecule combustion. Increasing this knowledge promises to be the best hope of achieving more robust optimized combustion chemistry mechanisms.

Conclusions

It is not possible to match experimental data for C_3 combustion by adjusting the rate parameters of C_3 elementary reactions while keeping the $C_{<3}$ rate parameters at values obtained by optimizing them to $C_{<3}$ combustion data alone. Instead, parameter optimization undertaken for the purpose of representing C_3 combustion data has to be carried out by matching data for the combustion of small- and intermediate-sized fuels simultaneously.

REFERENCES

1. Lissianski, V. V., Zamansky, V. M., and Gardiner Jr., W. C., in *Gas-Phase Combustion Chemistry,* Springer-Verlag, New York, 1999, pp. 1–123.
2. Smith, G. P., Golden, D. M., Frenklach, M., Eiteneer, B., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner Jr., W. C., Lissianski, V. V., and Qin, Z., http://www.me.berkeley.edu/gri_mech/ (1999).
3. Kee, R. J., and Miller, J. A., in *Complex Chemical Reaction Systems* (J. Warnatz and W. Jäger, eds.), Springer-Verlag, Berlin, 1986, pp. 196–221.
4. Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A., *A FORTRAN Program for Modeling Steady Laminar One-Dimensional Premixed Flames*, Sandia report SAND85-8240.
5. Davis, S. G., Law, C. K., and Wang, H., *Combust. Flame* 119:375–399 (1999).
6. Davis, S. G., Law, C. K., and Wang, H., *Proc. Combust. Inst.* 27:305–312 (1998).
7. Davis, S. G., Law, C. K., and Wang, H., *J. Phys. Chem. A* 103:5889–5899 (1999).
8. Seery, D. J., and Bowman, C. T., *Combust. Flame* 14:37–47 (1970).

9. Curran, H., Simmie, J. M., Dagaut, P., Voisin, D., and Cathonnet, M., *Proc. Combust. Inst.* 26:613–620; Curran, H., private communication, 1996.

10. Qin, Z., Yang, H., and Gardiner Jr., W. C., *Combust. Flame,* in press (2000).

11. Qin, Z., "Shock Tube and Modeling Study of Propane Ignition," dissertation, University of Texas at Austin, 1998.

12. Vagelopoulos, C. M., and Egolfopoulos, E. N., *Proc. Combust. Inst.* 27:513–519 (1998).

13. Egolfopoulos, F. N., Zhu, D. L., and Law, C. K., *Proc. Combust. Inst.* 23:471–478 (1990).

14. Gardiner Jr., W. C., Walker, B. F., and Wakefield, C. B., in *Shock Waves in Chemistry* (A. Lifshitz, ed.), Marcel Dekker, New York, 1981, pp. 319–374.

15. Ryu, S.-O., Hwang, S. M., and Rabinowitz, M. R., *J. Phys. Chem.* 99:13984–13991 (1995).

16. Lissianski, V. V., Yang, H., Qin, Z., Mueller, M. R., Shin, K. S., and Gardiner Jr., W. C., *Chem. Phys. Lett.* 240:57–62 (1995).

17. Vagelopoulos, C. M., Egolgopoulos, F. N., and Law, C. K., *Proc. Combust. Inst.* 25:1341–1347 (1994).

18. Wang, H., and Frenklach, M., *Combust. Flame* 110:173–221 (1997).